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(54) TEXTILE TREATMENT COMPOSITIONS

- (71) We, THE PROCTER & GAMBLE COMPANY, a Company organized and exist-
 ing under the laws of the State of Ohio, United States of America, of 301 East Sixth Street,
 Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for
 which we pray that a patent may be granted to us, and the method by which it is to be
 performed, to be particularly described in and by the following statement:

This invention relates to textile treatment compositions which are suitable for application
 to textile goods especially after washing, and which improve the appearance and handle of the
 finished laundered fabrics.

- One of the more tedious household tasks in connection with home laundering is ironing.
 This is usually carried out on cellulose fabrics such as cotton or linen, and on fabrics of
 cellulose fibres mixed with others such as polyester/cotton mixtures. The present invention
 facilitates the task of ironing and can enable ironed goods of improved appearance to be
 obtained with less wrinkling, with better resistance to subsequent wrinkling, and with
 "body". This last effect can also be observed on un-ironed fibres such as carpets or hair.

- It has long been known to use starch as an aid in achieving smooth wrinkle-free ironed
 fabrics, and it is known to use dextrans as textile sizing agents (of Industrial Gums, Second
 Edition, F.L. Whistler, 1973, p.598). However, starch renders fabrics stiff and harsh feeling.
 Further, starch and dextrans must be applied to the fabrics from relatively concentrated
 dispersions or solutions, only such starch or dextrin as is mechanically trapped in the fabric
 being available to exert the observed effect. The compositions of the invention avoid the
 harshness caused by starch treatments and permit dextrans to be applied from very dilute
 solutions. Thus preferably the compositions of the invention are intended to be formulated so
 as to be used as rinse additives, that is to be added to the final rinse water after a laundering
 operation; dextrin alone added in this way is almost wholly ineffective. The compositions can
 also, if desired, be formulated so as to be suitable for spraying on to garments before they are
 ironed, for instance, from an aerosol dispenser, or they may be in paste or granular form, or
 encapsulated and in the form of a dispersion of microcapsules, or they may be releasably
 associated with an insoluble rigid or flexible substrate.

- The present invention provides a textile-treating composition comprising (a) a fabric-
 substantive cationic surfactant and (b) a dextrin that is a substituted or unsubstituted
 pyrodextrin, a dextrin substituted by one or more anionic, nonionic or cationic substituents,
 or a mixture thereof.

The components of the present invention will be described in detail below.

The Dextrin

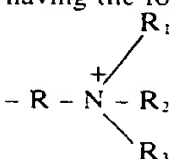
Dextrins are degradation products of starch, obtained by treatment of the starch in aqueous dispersion by hydrolysis or by enzymes or in substantially dry state by heat. The dextrins obtained by heat treatment of substantially dry starch are known as pyrodextrins. Their preparation and properties are described in "Starch: Chemistry and Technology, Vol. I, Fundamental Aspects 1965, especially Chapter XVIII, and Vol. II, Industrial Aspects 1967, especially Chapter XI" by R.L. Whistler and E.F. Paschall, published by Academic Press.

Dextrins generally have a molecular weight in the range from about 1,000 to 40,000, especially from 3,000 to 20,000. Preferred pyrodextrins are British gums, and white dextrins. Canary dextrins by themselves are much less effective, but mixtures of, for instance, white dextrins and canary dextrins, proportioned so as to have average properties similar to those of British gums, may be suitable for the invention. The dextrins may be made from starches of any sort, such as from maize, rice, barley, potato and other roots.

It is preferred that little or no undegraded starch be present in the compositions.

Pyrodextrins themselves can be used in the present invention and these materials, because of their ready availability and relative cheapness are preferred. Compositions of the invention can also employ a substituted dextrin by which is meant a dextrin, preferably a pyrodextrin, that has been substituted by one or more groups selected from cationic, anionic and nonionic groups.

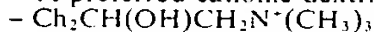
Preferred cationic dextrins for use in the present invention contain, per anhydro-glucose unit, from 0.001 to 1.5 substituents linked to an anhydro-glucose unit by an ether linkage and having the formula



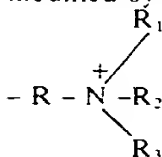
where R is an alkylene group optionally with a hydroxyl substituent; R₁ and R₂ are independently selected from C₁-C₄ alkyl groups; and R₃ is selected from hydrogen, C₁-C₄ alkyl and benzyl groups.

Cationic dextrins of the above type have not, as far as is known, been suggested for use in textile treatment compositions and these materials may provide some benefit on their own, although they are preferably used in the present invention in combination with another fabric-substantive cationic material.

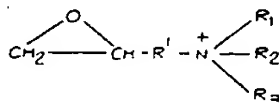
A preferred cationic dextrin has the substituent group:



To obtain the ether products which are useful for the invention, the dextrin may be modified by introducing the pendant group of formula



by any effective method. One method is to react the pyrodextrin with an epoxide of formula



where R' is an alkylene group having two fewer carbon atoms than R. One effective method of carrying out the addition of cationic epoxide (GMAC) to dextrin is similar in many ways to that recommended by the epoxide manufacturer (Shell Chemicals) for modification of starch (Shell) document entitled, "Starch Modification with GMAC", undated). Thus a weight ratio of dextrin to water varying between 1:1 and 1:2 may be used with enough sodium hydroxide to give a pH of 11.2 and the mixture stirred for a period ranging from 4 to 48 hours at temperatures ranging from 35-65°C. Dextrin-epoxide weight ratios have been varied between 10:1 to 1:2 depending on desired degree of substitution (D.S. values range between 0.05 and 1.5). With the larger amounts of epoxide it has been found advantageous to add the reagent portionwise to avoid overheating. For high D.S. products, isolation involves evaporation of the neutralised reacting mixture under reduced pressure and trituration with ethanol.

whilst for low D.S. products (0.25) the modified polysaccharide can be precipitated directly from the reaction mixture by addition of ethanol, washed with further ethanol and dried. For products of lighter colour a bleaching step may be included.

The compounds may also be prepared by reacting the dextrin with a quaternary ammonium salt in which one of the substituents on the nitrogen atom is a chloro-substituted alkyl group.

Compounds suitable for use according to the invention have a degree of substitution from about 0.001 to 1.5, preferably from about 0.01 to 1.0.

Other dextrans useful in the present invention are substituted either by anionic or by nonionic groups. Anionic substituents may be linked to the dextrin molecule by ester linkages at one of the hydroxyls of the anhydro-glucose units. Groups linked in this way include phosphates, which are preferred, carboxylates, and other inorganic acid groups such as sulphates and borates. Alternatively, acidic groupings may be ether-linked, e.g., OCH_2COOH groups and homologues thereof.

For preparing dextrin phosphates a modification may be used for a method for simultaneously phosphorylating and dextrinising starch described in United States Patent 3642774. Instead of starch as raw material, white dextrin may be used. Typically in this procedure the polysaccharide is intimately mixed with tetrasodium pyrophosphate, sodium dihydrogen phosphate and orthophosphoric acid in a little water and the mixture is first heated to 85°C for 2 hours under a slight vacuum (about 550mm. Hg.) and then at 140°C for 3 hours at 70mm. A neutralised solution of the product is subjected to ultrafiltration to remove unbound phosphate and evaporated to dryness. This method produces dextrin phosphates of good colour, of D.S. approaching 0.2. The second method described in United States Patent 3320237 leads to higher D.S. values. Again dextrin has been used as raw material rather than starch. In this method the polysaccharide is filtered from a saturated solution of sodium dihydrogen phosphate and the wet filter cake is dried and heated at 140°C for 7 hours in a vacuum oven. After the usual ultrafiltration steps to remove unbound phosphate, the products are found to have D.S. values in the range from 0.3 to 0.6.

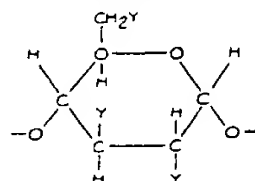
Another preferred anionic dextrin is the ether of dextrin with hydroxymethyl pyrrolidone carboxylic acid or their salts.

These materials are novel compounds and the corresponding derivatives of starch can also be used to treat fabrics.

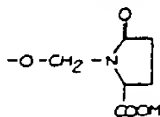
These materials have the additional property of tending to increase the residual moisture level in "dry" fabrics.

The new compounds comprise dextrin or starch combined by an ether linkage at at least some of its constituent anhydroglucose units to N-hydroxymethyl-2-pyrrolidone-5-carboxylic acid or its salts. The degree of substitution (D.S.) is from 0.01 to 2, preferably 0.01 to 1, more preferably 0.2 to 0.7.

The substituted anhydroglucose units are believed to have the formula



wherein on average a total of 0.01 to 2 Y's represent the group



and the remainder represent $-\text{OH}$, and M represents an anion, preferably sodium or potassium.

When these compounds are made, the P.C.A. group may be attached to any or all of the hydroxyl positions Y to varying extents. Although a D.S. of 3 is theoretically possible, in practice a D.S. of 2 is the highest obtainable.

The compounds may be prepared by hydroxymethylating P.C.A. by reaction with formaldehyde in the presence of a basic catalyst, recovering the product and reacting it with dextrin or starch in the presence of metal and acid catalysts.

The method is based on a process described in Textile Res. J., 1975, 354 (J.D. Turner) for adding 2-pyrrolidone-5-carboxylate to cellulose. In the present method, initially the P.C.A. is treated with a slight excess (1.05 to 1.15 molar proportion) of formaldehyde in strong (50%) aqueous solution using sodium hydroxide (to pH9-10) as catalyst. The solution of

N-hydroxymethyl - P.C.A. thus formed is intimately mixed with dextrin. British gum or starch (the amount depending on the desired D.S.) in the presence of metal (eg. zinc nitrate) and acid (acetic acid) catalyst, and the paste so formed is evaporated to dryness under reduced pressure. The condensation reaction is carried out by heating in the fan oven at 140-160°C. That bonding of the P.C.A. to the polysaccharides had taken place was demonstrated by ultrafiltration experiments in which it was shown that degree of substitution, measured either by nitrogen analysis or potentiometric titration of carboxyl groups, was not sensibly decreased even after 24 hours filtration through a membrane permeable to species with MW < 1000.

Nonionic substituents are usually linked by an ether grouping to the anhydroglucose units, and others such as those with C₁₋₄ alkyl and 2-hydroxyalkyl groups are suitable. Hydroxy ethyl and hydroxy propyl British gums are preferred, especially the latter which has somewhat better performance and requires less volatile raw material in its manufacture. The 2-hydroxyalkyl ethers may be prepared by reacting dextrin with an appropriate epoxy compound such as propylene oxide.

Thus hydroxypropyl derivatives may be prepared by use of a slight modification of the method applicable to starch, described by Kester and Hjermstad in "Methods in Carbohydrate Chemistry" Vol.4, p. 304. Preferably water (2 vols.) is used as solvent rather than isopropanol. Essentially the method involves heating the dextrin in twice its weight of water with moderate excess of epoxide (30 to 40%) over that theoretically required to give the desired D.S., under alkaline conditions in a closed vessel at 50°C for 48 hours. The products may be isolated by evaporation under reduced pressure and washing with ethanol or by precipitating with industrial methylated spirit. Their colour may be improved by bleaching with hydrogen peroxide. The degree of substitution may be about 0.5.

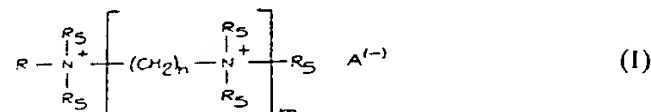
The degree of substitution of the dextrin, ie. the average number of substituent groups combined per anhydroglucose unit in the dextrin, is usually in the range 0.001 to 1.5, preferably 0.05 to 1.0, and especially about 0.1-0.5.

The Cationic Surfactant

Very many fabric substantive cationic surfactants are known in the art, and almost any cationic surfactant having at least one long chain alkyl group of about 10 to 24 carbon atoms in the molecule is suitable; such compounds are described in "Cationic Surfactants", Jungermann 1970.

Some compounds of this class include compounds from the group consisting of

- (i) non-cyclic quaternary ammonium salts having at least one C₁₂₋₃₀ alkyl chain,
- (ii) substituted polyamine salts of formula



wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R₅'s which may be the same or different each represent hydrogen, a (C₂H₄O)_pH or (C₃H₆O)_qH, or a C₁₋₃ alkyl group, where each of p and q is a number such that (p + q) does not exceed 25, m is from 1 to 9, n is from 2 to 6, and A⁽⁻⁾ represents one or more anions having total charge balancing that of the nitrogen atoms.

(iii) polyamine salts having the formula I where R is hydrogen or a C₁₋₄ alkyl group, each R₅ is hydrogen, or a C₁₋₄ alkyl group, n is from 2 to 6 and m is not less than 3,

(iv) C₈₋₂₅ alkyl imidazolinium salts,

(v) C₁₂₋₂₀ alkyl pyridinium salts, and

It will be understood that the main function of the cationic surfactant is to encourage deposition of the dextrin derivative and it is not, therefore, essential that the cationic surfactant itself have substantial softening properties, although this may be the case. Indeed, it is somewhat preferred that at least a part of the cationic component of the composition comprises a surfactant having only a single alkyl chain, as such compounds have greater solubility in water and can more effectively provide the appropriate positive charge distribution and the degree of hydration on the surface of the emulsified nonionic softener particle.

Thus, it is preferred that a cationic surfactant having a single C₁₂-C₂₂, preferably C₁₄-C₁₈, alkyl group should be present.

Highly preferred cationic surfactants of class (i) are the quaternary ammonium salts of the formula

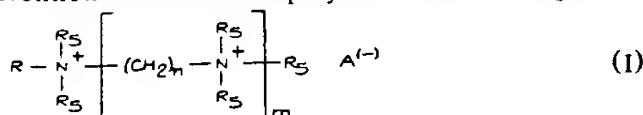


Wherein group R₁ is C₁₂-C₂₂, preferably C₁₆-C₁₈ fatty alkyl and groups R₂, R₃ R₄ are each C₁-C₄ alkyl, preferably methyl, and the counterion A is as above.

The conventional quaternary ammonium softening agents of the above formula wherein R₁ and R₂ are each C₁₂-C₂₀ fatty alkyl and R₃ and R₄ are each C₁-C₄ alkyl, function in the

same way as the preferred single long alkyl chain compounds, but preferably in the present invention such softening agents are used in conjunction with the preferred cationic surfactants.

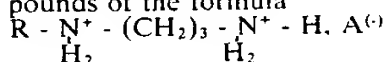
Also useful in the present invention are substituted polyamine salts of the general formula



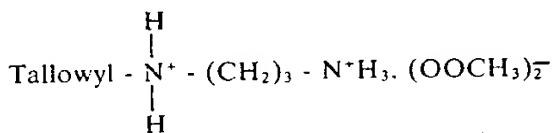
wherein R is an alkyl or alkenyl group having from about 10 to 22, preferably from 12 to 20, especially from 16 to 18 carbon atoms, the groups R_S which may be the same or different each represent hydrogen, a (C₂H₄O)_pH or (C₃H₆O)_qH or a C₁-C₃ alkyl group where each p and q is a number such that (p + q) does not exceed 25, n is an integer from 2 to 6, preferably 3, m is from 1 to 9, preferably from 1 to 4, and A⁽⁻⁾ represents one or more anionics having total charge balancing that of the nitrogen atoms. The group R may also be a C₁₀-C₁₂ alkyl group interrupted by a bivalent functional group, for example an ether linkage.

These polyamine salts can, in certain circumstances, provide additional positive charge to the particle and thereby improve deposition.

The mono-substituted derivatives of 1,3-diaminopropane are very effective, that is compounds of the formula



wherein R is as described above, and preferably is predominantly C₁₆₋₁₈ alkyl, derived from tallow fatty acids. Diaminopropane may also be named propylene diamine. Optionally the N-hydrogen atoms may be ethoxylated with up to 25 ethoxy groups in all. When ethoxylated preferably from 3 to 6 ethoxy groups in all are employed. A⁽⁻⁾ may represent a dihalide or any appropriate acidic radical such as the diacetate, or higher saturated or unsaturated acyl groups up to C₂₂. A preferred compound of this class is believed to have the formula

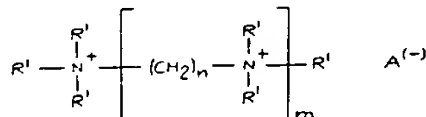


and is sold under the trade names Dinoramac (Messrs Pierrefitte-Auby) or Duomac (Messrs Armour-Hess), or more preferably the corresponding halide, especially chloride. "Tallowyl" represents the predominantly C₁₆ to C₁₈ alkyl groups derived from tallow fatty acids. A very highly preferred material is the ethoxylated derivative of this compound having a total of 3 ethoxylate groups per molecule.

The unprotonated amine may also be used to prepare the compositions but it is highly preferred for a good product performance that their pH be such that at least one of the amine groups of the polyamine is present in them, or at least in the treatment bath, in protonated form.

Preferred is a diquatary ammonium salt having the chemical name: N-tallow-N,N,N',N'-pentamethyl-1,3-propylene diammonium dichloride, which is commercially available under the trade names STABIRAN MS-3 (Pierrefitte-Auby); DUO-QUAD (Armour-Hess); and ADOGEN 477 (Ashland Co.), or N-tallow-N,N',N'-triethanol-1,3-propylenediamine hydrochloride.

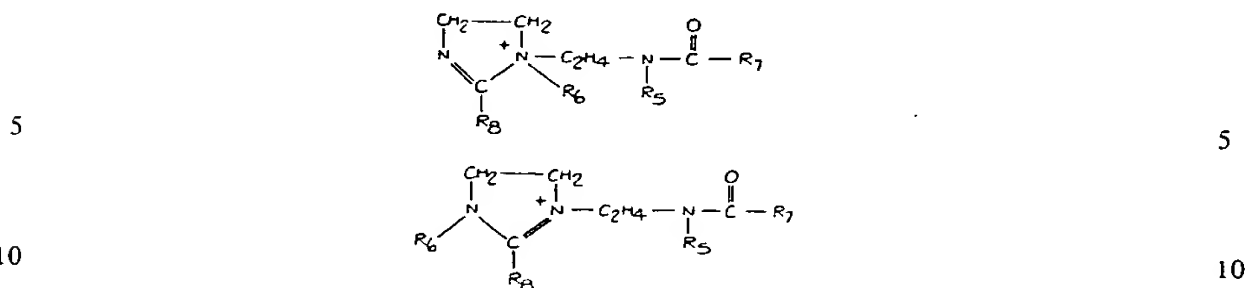
Another class of suitable cationic surfactants herein includes polyamine salts (also frequently termed polyalkylene imine salts), if desired substituted, which can be represented by the formula



wherein R' represents hydrogen or a C₁-C₄ alkyl group, n is an integer from 2 to 6, preferably from 2 to 4, most preferably 2, m is not less than 3, preferably from 6 to 24, especially from 8 to 16.

A preferred compound of this class is for instance a polyethylene iminium chloride containing about 10 ethylene imine units.

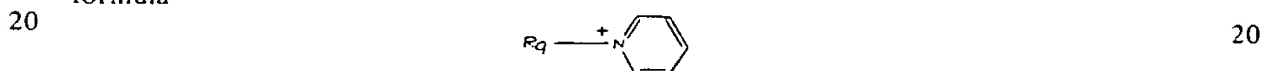
Alkyl imidazolinium salts of class (iv) useful in the present invention are generally believed to have cations of the general formula



wherein R_5 is hydrogen or a C_1 - C_4 alkyl radical, R_6 is a C_1 - C_4 alkyl radical, R_7 is a C_9 - C_{25} alkyl radical and R_8 is hydrogen or a C_8 - C_{25} alkyl radical.

A preferred member of this class is believed to have R_6 methyl and R_7 and R_8 tallow alkyl, R_5 hydrogen, and is marketed under the Trade Name Varisoft 455 by Ashland Chemical Company, Ohio, USA. Also suitable are the imidazolinium softeners described in pending U.K. patent application No. (21117/77) Serial No. 1574496)

Alkyl pyridinium salts of class (v) useful in the present invention have cations of the general formula



wherein R_9 is a C_{12} - C_{20} alkyl radical. A typical useful material of this type is cetyl pyridinium chloride.

Mixtures of more than one cationic surfactant may be employed. In the context of this invention, the broad terms "alkyl" and "alkenyl" are intended to encompass hydrocarbon radicals which are substituted or interrupted by functional groups.

The relative proportions of the dextrin material and the cationic surfactant in the compositions of the invention may vary over a wide range, for instance from about 50:1 to 1:50 by weight. Preferably the ratio is from 10:1 to 1:10 especially from 3:1 to 1:3. The actual concentrations of these components in the compositions depend upon the extent to which they are designed to be diluted in treatment bath or solution. Thus, lower concentrations might be used in a product intended to be sprayed on to garments without further dilution, than in a product intended to be much diluted when used in a rinse bath.

Rinse additive compositions used at low concentrations have become widely employed as textile softeners in recent years, and the amount to be used has become conventional. If the present compositions are intended to be used in a rinse in these now conventional amounts, a concentration of about 0.5% to 10% dextrin and 1 to 10% cationic surfactant is suitable. Of course, products intended to be used in smaller amounts would be more concentrated. In the actual treatment bath eg. the rinse liquor, a concentration of from about 10 parts per million (ppm) to about 0.1% preferably about 50 to 500 ppm by weight of dextrin and cationic surfactant together is appropriate. Higher concentrations may be used in compositions intended to be sprayed on to fabrics, for instance up to 10% or more.

Optional Components

In addition to the dextrin and cationic surfactant the compositions may contain small amounts of nonionic surfactants as emulsifiers for the cationic or dextrin or other components. In particular, however, they may contain nonionic components, not necessarily surfactants, having beneficial effects upon the fabrics to be treated or in the ironing operation.

Such additives include those described in German Offenlegungsschrift No. 2,631,114. These agents are fatty acid esters of mono- or polyhydric alcohol or anhydride thereof, said alcohol or anhydride having from 1 to 8 carbon atoms. It is preferred that the fatty acid ester has at least 1, more preferably at least 2, free (ie. unesterified) hydroxyl groups and at least 1, more preferably at least 2, fatty acyl groups.

The mono- or polyhydric alcohol portion of the ester can be represented by methanol, isobutanol, 2-ethylhexanol isopropanol, ethylene glycol and polyethylene glycol with a maximum of 5 ethylene glycol units, glycerol, diglycerol, xylitol, erythritol, pentaerythritol, sorbitol or sorbitan. Ethylene glycol, glycerol and sorbitan esters are particularly preferred.

The fatty acid portion of the ester normally comprises a fatty acid having from 12 to 22 carbon atoms, typical examples being lauric acid, myristic acid, palmitic acid, stearic acid and behenic acid.

One highly preferred group of softening agents for use in the present invention is the sorbitan esters, which are esterified dehydration products of sorbitol.

Other fatty acid partial esters useful in the present invention are xylitol monopalmitate, pentaerythritol monostearate, glycerol monostearate and ethylene glycol monostearate. As with the sorbitan esters, commercially available mono-esters normally contain substantial

quantities of di- or tri-esters.

The glycerol esters are also highly preferred. These are the mono-, or tri-esters of glycerol and fatty acids of the class described above. Commercial glycerol monostearates, is especially preferred.

5 In rinse additive compositions a content of from about 1 to about 10% preferably from 1.5 to 6% by weight of nonionic textile conditioning agent is usually suitable. 5

In addition to or instead of the above described nonionic components the compositions may contain other textile treatment or conditioning agents. Such agents include silicones. Some suitable silicones are predominantly linear polymers, that is they are poly dialkyl- or 10 diaryl siloxanes. The alkyl groups have 1 to 5 carbon atoms, and are preferably methyl. The alkyl groups may be wholly or partially fluorinated. A limited degree of cross linking can be tolerated, and up to about 10% by weight of mono-alkyl siloxanes may be present in the silicones. 10

Preferred silicones are poly dimethyl siloxanes having viscosity at 25°C in the range 100 to 200000 centistokes, preferably 1000 to 120000. Other preferred silicones are fluorinated 15 silicones having viscosity at 25°C of at least 100 centistokes and cationic silicones, both of which are described in German Offenlegungsschrift No. 2,631,419. These silicones are either (a) A predominantly linear di C₁-C₅ alkyl or C₁-C₅ alkyl, aryl siloxane having a viscosity at 25°C of at least 100 centistokes, prepared using a cationic surfactant as emulsifier. 15

(b) An α,β -di quaternised di C₁-C₅ alkyl or C₁-C₅ alkyl aryl silicone polymer, or 20 (c) An amino functional di C₁-C₅ alkyl or alkyl aryl siloxane polymer in which the amino group may be substituted and may be quaternised and in which the degree of substitution (d.s.) lies in the range 0.001 to 0.1, preferably 0.01 to 0.07. 20

The silicone component is preferably used in an amount of from about 0.5% to about 10%, 25 most preferably from 1% to 6% of the softener composition. In other preferred executions of this invention the weight ratio of the sum of nonionic conditioning substance and silicone to cationic surfactant is in the range from 4:1 to 1:2. Of course, where other nonionic components such as these are present the ratio of modified dextrin to cationic surfactant in the compositions may be towards the lower end of the effective ranges. 25

30 A preferred composition of the present invention incorporating these additives comprises by weight 30

(a) from 2 to 10% pyrodextrin selected from British gum and white dextrin, (b) from 1 to 10% of a cationic selected from one or more of ditallow dimethyl ammonium chloride, N-tallow-1,3-propylenediamine hydrochloride, N- 35 tallow-N,N,N',N'-pentamethyl-1,3-propylene diammonium dichloride and N-tallow-N,N',N'-tri-ethanol-1,3-propylene diamine hydrochloride. 35

(c) from 1 to 10% of glycerol monostearate or sorbitan monostearate, (d) from 1 to 4% of a polydimethyl siloxane of viscosity at 25°C in the range from 1000 to 120000 centistokes. 40

Other components appropriate to the type of compositions being formulated may also be present. Such components are preservatives, bactericides, whether effective to protect the composition or to treat fabrics, viscosity controllers, colouring and perfuming materials and the like. 40

The following are examples of the invention. All percentages are given by weight of the composition. 45

Examples 1-12 define compositions of the invention employing pyrodextrin. The following compositions were prepared by dispersing molten DTDMAC and the other ingredients in water.

| | | <i>Examples</i> | | | | |
|----|---|-----------------|----------|----------|----------|----------|
| | <i>Ingredients</i> | <i>1</i> | <i>2</i> | <i>3</i> | <i>4</i> | <i>5</i> |
| | | % | % | % | % | % |
| 5 | Ditallow dimethyl ammonium chloride (DTDMAC) | 4 | 6 | 4 | 6 | 6 |
| 10 | White Dextrin (m.wt. 5000) | 2 | 2 | 3 | - | - |
| | British gum (m.wt. 5000) | - | - | - | 3 | 1.5 |
| 15 | Glycerine monostearate | - | - | 2 | - | - |
| | Polydimethyl siloxane (viscosity 4000 c.s. at 25°C) | - | - | - | - | 1.5 |
| 20 | Water | | | | | |
| | | | | | to 100 | |
| 25 | Each composition was used in the form of a dilute solution, and fabrics that were rinsed in each solution and then dried were easier to iron and had a better ironed appearance (smoothness, lack of wrinkles) than fabrics rinsed in similar solutions from which the dextrin was omitted. | | | | | |
| 30 | Similar results are obtained when the DTDMAC is replaced by a 50/50 mixture of DTDMAC and dodecyl trimethyl ammonium bromide, by cetyl trimethyl ammonium bromide, by cetyl pyridinium chloride, by DUOQUAD (trade name), VARISOFT 455 (trade name), by ADOGEN 477 (trade name) or by polyethylene imine chloride containing 10 ethylene imine units. | | | | | |
| 35 | Similar results are obtained if the British gum is replaced by a half and half mixture of Canary dextrin and white dextrin. | | | | | |
| | Similar results are obtained if the glycerine monostearate is replaced by sorbitan monostearate, ethylene glycol monostearate, diglycerol monotallowate, xylitol monopalmitate or a 1:2 molar mixture of glycerol tristearate and glycerol monostearate. | | | | | |
| | Further examples of compositions containing pyrodextrin are as follows: | | | | | |

| | | Examples | | | | | | |
|---|---|----------|----|----|-----|-----|----|----|
| Ingredients | | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| 5 | | % | % | % | % | % | % | % |
| | DTDMAC | 4 | - | 3 | 6 | - | 2 | - |
| 10 | Cetyltrimethylammonium bromide | - | 8 | - | - | - | - | - |
| | N-tallow-N,N',N'-triethanol-1,3-propylene diamine hydrochloride | - | - | - | 2 | - | - | - |
| 15 | N-tallow-N,N',N'-triethoxy-ethanol-1,3-propylene diamine hydrochloride | - | - | 4 | - | 6 | 4 | 8 |
| 20 | British gum (m. wt. 5000) | - | - | 2 | 3 | 1.5 | - | - |
| | British gum (m. wt. 20,000) | - | 1 | - | - | - | 2 | 4 |
| | Canary dextrin | 2 | 1 | 1 | - | - | - | - |
| 25 | White dextrin | - | - | - | - | 1.5 | - | - |
| | Polydimethylsiloxane | - | - | 1 | - | - | 2 | - |
| 30 | Water | to 100 | | | | | | |
| Examples of nonionic and anionic modified dextrans are as follows: | | | | | | | | |
| Example 13 | | | | | | | | |
| 35 | Cotton fabrics were steeped in a rinse bath containing 0.3% by weight of a textile-conditioning composition consisting of 6% DTDMAC and 2% hydroxypropyl dextrin (D.S. 0.06) in water. After drying the fabrics were ironed and were found to be easier to iron and more flat, smooth and free from wrinkles when ironed than fabrics similarly treated with a composition containing 6% DTDMAC only. | | | | | | | |
| 40 | Similar results were obtained when the hydroxypropyl dextrin was replaced by phosphated dextrin (D.S. 0.25). | | | | | | | |
| Examples 14-17 | | | | | | | | |
| The following compositions were prepared | | | | | | | | |
| 45 | | 14 | 15 | 16 | 17 | | | |
| | DTDMAC | 6 | 4 | 2 | 0.7 | | | |
| | Dextrin etherified by N-hydroxy methyl-2-pyrrolidone-5-carboxylic acid (D.S. 0.48) | 2 | 2 | 2 | 2 | | | |
| 50 | Water | to 100 | | | | | | |
| Example 18 | | | | | | | | |
| 55 | A textile treatment composition in the form of an emulsion comprised: | | | | | | | |
| | 3% DTDMAC | | | | | | | |
| | 1.5% Hydroxypropyl British gum (D.S. 0.55; m.wt. 5000) | | | | | | | |
| | 1.5% Polydimethyl siloxane (viscosity 4000 centistokes at 25°C. polymerized in the presence of DTDMAC) | | | | | | | |
| 60 | Balance: Water | | | | | | | |
| This composition provided ease of ironing and ironing end result. | | | | | | | | |
| Similar results are obtained when the DTDMAC in the above formula is replaced by ditallow dimethyl ammonium methosulphate, by 1:1 mixture of DTDMAC and cetyl trimethyl ammonium bromide, by cetyl pyridinium chloride, by DUOQUAD (trade name), by VARISOFT 455 (trade name), ADOGEN 477 (trade name), by polyethylene imine | | | | | | | | |

chloride containing 10 ethylene imine units, or by N-tallow-N,N',N'-triethoxyethanol-1,3-propylene diamine hydrochloride.

Substantially similar results were obtained when the hydroxypropyl dextrin was replaced by hydroxyethyl dextrin, but the former was slightly preferred.

5 *Example 19*

A textile treatment composition is prepared comprising
1.5% Ditallow dimethyl ammonium chloride (DTDMAC)
1.5% Cetyl trimethyl ammonium chloride
1.5% Hydroxypropyl British Gum
10 1.5% Polydimethyl siloxane (as in Example 6)
2.0% Glycerine monostearate
Balance Water

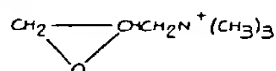
It was made by mixing the hydroxy propyl British gum and a melt of the other components into the water.

15 In this composition the glycerine monostearate may be replaced by sorbitan monostearate, ethylene glycol monostearate, diglycerol monotallowate, xylitol monopalmitate or a 1:2 molar mixture of glycerol tristearate and monostearate.

Fabrics sprayed with the compositions and then ironed were found to be more flat, smooth and free from wrinkles than similar fabrics sprayed with an equal amount of water.

20 *Examples 20 and 21*

An aqueous textile treatment composition was prepared containing 6% ditallow dimethyl ammonium chloride (DTDMAC), 2% white dextrin (molecular weight about 5000) reacted with an epoxy compound of formula



25 to a degree of substitution (Example 20) of 0.15 and (Example 21) of 0.26. The counterion of the cationic dextrin was chloride. The composition was prepared by mixing the molten DTDMAC and dextrin product in water. Pillow cases rinsed in dilute solutions of these 30 compositions were found to be easier to iron and to have a more pleasing appearance than those treated by similar compositions lacking the modified dextrin. Similar results were obtained when the counterion of the cationic dextrin was lactate. Similar performance is obtained when half the DTDMAC is replaced by didecyltrimethyl ammonium bromide, or 35 when all of it is replaced by cetyl trimethyl ammonium bromide, cetyl pyridinium chloride, DUOQUAD (trade name), VARISOFT 455 (trade name), ADOGEN 477 (trade name), polyethylene imine chloride containing 10 polyethylene imine units or N-tallow-N, N',N'-triethanol-1, 3-propylenediamine hydrochloride.

Examples 22 and 23

40 Compositions were prepared containing 6% by weight of (22) white dextrin (molecular weight about 5000) reacted as in Example 20 to a degree of substitution of 0.46 and of (23) British gum (molecular weight about 5000) reacted likewise, with 94% water.

Similar results are obtained when the British gum is replaced by a half and half mixture of white dextrin and Canary dextrin.

45 *Example 24*

A textile treatment composition was prepared consisting of an aqueous emulsion comprising by weight:

3% Ditallowdimethyl ammonium chloride (DTDMAC)
1.5% Cationic silicones
50 1.5% Cationic British gum
0.25% Tergitol 15-5-9
Balance water.

The cationic silicone was prepared by polymerising dimethyl siloxane in the presence of DTDMAC (weight ratio siloxane:DTDMAC 10:1) and of a little tetra butyl ammonium chloride (siloxane:tetra butyl ammonium chloride 100:1) at 100°C. The silicone had viscos- 55 ity of 4000 centistokes.

The cationic British Gum was British gum combined with -CH₂CH(OH)CH₂N⁺(CH₃)₃ to a degree of substitution of 0.1.

60 Tergitol (trade mark) 15-S-9 is a trade name for the product of the condensation of C₁₁-C₁₅ secondary linear alcohols with 9 molar proportions of ethylene oxide.

Example 25

A textile treatment composition is prepared comprising
3% Ditallowdimethylammonium chloride
1.5% Cationic Silicone (as in Example 6).
65 1.5% Cationic British Gum (MWt 5000 D.S. 0.05).

1.5% Glycerine monostearate.

Balance water.

It is made by mixing the cationic British gum and a melt of the other components in to the water.

- 5 The glycerine monostearate may be replaced by sorbitan monostearate, ethylene glycol monostearate, diglycerol monotallowate, xylitol monopalmitate or a 1:2 molar mixture of glycerol tristearate and monostearate.

Examples 26-29

- 10 Pyrrolidonecarboxylic acid (23.9g) is dissolved in sufficient strong caustic soda solution to make a 50% aqueous solution of the sodium salt (P.C.A.). This is mixed with 37% formaldehyde solution (17.3g) and the pH is adjusted to 9.5 with 50% aqueous sodium hydroxide. After overnight storage at room temperature the pH is adjusted to 4.6.

- 15 To a portion (30g) of this solution is added a white dextrin (20g, Sigma Chemical Co., molecular weight about 5000), catalyst X4 (a zinc nitrate solution from Sun Chemical Co., 2g), Sulphanol 550 (a nonionic emulsifier from Sun, 0.06g) and acetic acid (0.3g), and the mixture is stirred to a paste. This is evaporated to dryness under reduced pressure and the residue is heated in a fan oven, firstly at 100°C (5 mins) and then at 150°C (5 mins), and ground to a powder.

- 20 Potentiometric titration of a sample (0.5g) from pH7 to 2 indicated a carboxyl content consistent with a degree of substitution (D.S.) of the dextrin of 0.48. Analysis for nitrogen content led to a similar result. Ultrafiltration in distilled water through a UM2 membrane (Amicon) for 24 hours did not give rise to a significant lowering of D.S.

This material was used to prepare the following compositions:

| | | | | | | |
|----|--|--------|----|----|-----|----|
| 25 | <i>Ingredients</i> | 16 | 27 | 28 | 29 | 25 |
| | | % | % | % | % | |
| 30 | Ditallow dimethyl ammonium chloride (DTDMAC) | 6 | 4 | 2 | 0.7 | 30 |
| | Dextrin P.C.A. | 2 | 2 | 2 | 2 | |
| 35 | Water | to 100 | | | | 35 |

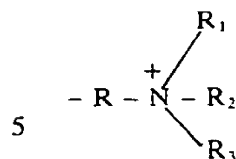
The compositions were prepared by mixing the molten DTDMAC and the dextrin product in the water.

- 40 When fabrics were steeped in 0.4% by weight solutions of these products in water, dried and ironed, all gave better ironing end result than corresponding fabrics steeped in water and composition 4 was preferred.

- 45 Substantially similar results are obtained if the DTDMAC is replaced by ditallow dimethyl ammonium methosulphate by a 1:1 mixture of DTDMAC and cetyl trimethyl ammonium bromide, by cetyl pyridinium chloride, by Duoquad (Trade name), by Varisoft 455 (Trade name), by Adogen 477 (Trade name), by polyethylene imine chloride containing 10 ethylene imine units, or by N-tallow-N,N',N'-triethanol-1,3-propylene diamine hydrochloride.

WHAT WE CLAIM IS:

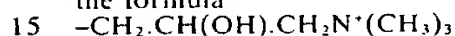
1. A textile-treating composition comprising (a) a fabric-substantive cationic surfactant and (b) a dextrin that is substituted or unsubstituted pyrodextrin, a dextrin substituted by one or more anionic, nonionic or cationic substituents, or a mixture thereof.
2. A composition as claimed in Claim 1 wherein the dextrin has a molecular weight of from 1,000 to 40,000.
3. A composition as claimed in Claim 1 or Claim 2 wherein the molecular weight of the dextrin is from 3,000 to 20,000.
4. A composition as claimed in any one of Claims 1-3 wherein the weight ratio of dextrin to cationic surfactant is from 1:10 to 10:1.
5. A composition as claimed in Claim 4 in which the said weight ratio is from 3:1 to 1:3.
6. A composition as claimed in any one of Claims 1-5 wherein the dextrin is a pyrodextrin selected from British gum and white dextrin.
7. A composition as claimed in any one of Claims 1-5 wherein the dextrin has, per anhydroglucose unit, from 0.001 to 1.5 cationic substituents of the formula



in which R is an alkylene group optionally with a hydroxyl substituent; R₁ and R₂ are independently selected from C₁-C₄ alkyl groups; and R₃ is selected from hydrogen, C₁-C₄ alkyl groups and a benzyl group, the cationic substituent being attached to the anhydroglucose unit by an ether linkage.

8. A composition as claimed in Claim 7 wherein the dextrin is a pyrodextrin.

9. A composition as claimed in Claim 7 or Claim 8 wherein the cationic substituent has the formula



10. A composition as claimed in any one of Claims 1-5 wherein the dextrin is substituted by an anionic grouping.

11. A composition as claimed in Claim 10 wherein the dextrin is substituted by one or more of phosphate, carboxylate, sulphate, and borate radicals.

12. A composition as claimed in Claim 10 wherein the dextrin is linked by an ether linkage at at least some of its constituent anhydroglucose units to N-hydroxymethyl-1-pyrrolidone-5-carboxylic acid or its salts.

13. A composition as claimed in any one of Claims 1-5 wherein the dextrin is substituted by a nonionic grouping.

14. A composition as claimed in Claim 13 wherein the nonionic grouping is a C₁-C₄ hydroxyalkyl group.

15. A composition as claimed in any one of Claims 10-14 wherein the degree of substitution of the dextrin is from 0.001 to 1.5.

16. A composition as claimed in any one of Claims 10-15 wherein the dextrin is a pyrodextrin.

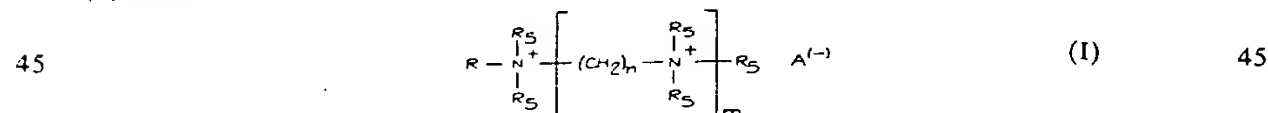
17. A composition as claimed in Claim 16 wherein the dextrin is white dextrin or British gum.

18. A composition as claimed in any one of Claims 7-17 wherein the degree of substitution is from 0.05 to 1.

19. A composition as claimed in Claim 18 wherein the degree of substitution is from 0.2 to 0.7.

20. A composition as claimed in any one of Claims 1-19 wherein the fabric-substantive cationic compound is selected from

- (i) non-cyclic quaternary ammonium salts having at least one C₁₂-C₃₀ alkyl chain.
 (ii) substituted polyamine salts of formula



wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R₅'s which may be the same or different each represent hydrogen, a (C₂H₄O)_pH or (C₃H₆O)_qH, or a C₁-C₃ alkyl group, where each of p and q is a number such that (p + q) does not exceed 25, m is from 1 to 9, n is from 2 to 6, and A⁽⁻⁾ represents one or more anions having total charge balancing that of the nitrogen atoms.

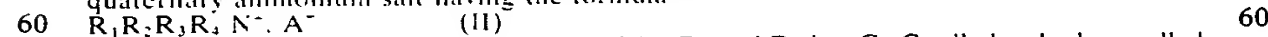
(iii) polyamine salts having the formula (I) wherein R is hydrogen or a C₁-C₄ alkyl group, n is from 2 to 6 and m is not less than 3.

(iv) C₈-C₂₄ alkyl imidazolium salts.

(v) C₁₂-C₂₀ alkyl pyridinium salts, and

(vi) mixtures of any two or more of these.

21. A composition as claimed in Claim 20 wherein the cationic compound is a non-cyclic quaternary ammonium salt having the formula



wherein R₁ is a C₁₂-C₂₂ alkyl group, each of R₂, R₃ and R₄ is a C₁-C₄ alkyl or hydroxy alkyl group and A is an anion.

22. A composition as claimed in Claim 20 wherein the cationic compound is a dialkyl quaternary ammonium compound of formula (II) wherein R₁ and R₂ are each C₁₂-C₂₀ alkyl, R₃ and R₄ are each C₁-C₄ alkyl and A is an anion.

23. A composition as claimed in Claim 20 wherein the cationic compound is a substituted polyamine salt of formula (I) wherein R is a $C_{12}-C_{20}$ alkyl group, m is 1, n is 3, A(-) is an anionic radical having two negative charges and each R_3 is hydrogen, a C_1-C_3 alkyl group, or an ethoxy group containing 1 or 2 ethylene oxide units.

5 24. A composition as claimed in any one of Claims 1-23 comprising an aqueous solution or dispersion containing from 0.1 to 10% by weight of the dextrin and from 1 to 10% by weight of the cationic surfactant. 5

25. A composition as claimed in any one of Claims 1-24 comprising an additional component selected from nonionic textile softeners and nonionic fibre lubricants.

10 26. A composition as claimed in Claim 25 comprising a textile softener that is a fatty acid ester of a C_1-C_8 mono- or polyhydric alcohol or the anhydride thereof. 10

27. A composition as claimed in any one of Claims 1 to 26 which also contains a silicone.

28. A textile-treating composition substantially as hereinbefore described with reference to any one of the examples.

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